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Synthesis, Characterization, and Functionalization of Hyperbranched Poly(ether ether ketone)s with Phenoxypheyl Side Group

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Novel fluoride-teminated hyperbranched poly(ether ether ketone) with 4-phenoxyphenyl side group (HPEEK-F) was prepared from 2-(4-phenoxyphenyl)-1,4-diphenol (A_2) and 1,3,5-tris[4-(4-flourobenzoyl) phenoxy]benzene (B_3). An end-capping approach was used to synthesize tertiary amino-terminated fluorescent (HPEEK-DMA) and phenyl ethynyl-terminated self-crosslinking poly(ether ether ketone)s (HPEEK-PEP). These three polymers have the same backbone structure and degree of branching ($DB = 0.67$), and different terminal groups. The nature of the terminal group was shown as the influences of the glass transition temperature (T_g) and decomposition temperature (T_d) of polymers. The T_g of HPEEK-F and HPEEK-DMA are 30°C lower than HPEEK-PEP, whereas the T_d of HPEEK-F are 90°C and 50°C higher than HPEEK-DMA and HPEEK-PEP, respectively. The HPEEK-DMA fluoresce blue-green in solid and in solution. This kind of hyperbranched polymer contains a large amount of terminal chromophore groups which can easily lead to the formation of intramolecular excimers. The fluorescence signal was decreased with increasing acidity, furthermore, the two peaks at 466 nm and 507 nm indicated a blue shift occurred. After curing, the HPEEK-PEP displayed a T_g at 235.5°C, which is 100°C higher than original polymers. Thermally cured samples show good anti-chemical corrodibility in DMF, THF, DMAc and NMP solvents.

Keywords: hyperbranched poly(ether ether ketone) (HPEEK); $A_2 + B_3$; end-cap; fluorescence; self-crosslinking

1. Introduction

Over the past 15 years, hyperbranched polymers have received much attention due to their unique chemical and physical properties, such as low solution and melt viscosities, high solubility and lack of chain entanglements. These attribute to their globular structure, and the presence of many terminal groups, which can be carried on for further reactions and functionalizations (1, 2). Hyperbranched polymers not only a play role as bulk materials in rheology modifiers, processing additives, and coating potential applications (3–7), but also as functional materials in optical waveguides (8–10), non-linear optical polymers (11, 12), magnetic polymeric materials (13, 14), catalysts, sensors, and nanotemplating material applications etc (2, 15–17).

Usually, the functional hyperbranched polymers are prepared from functional monomers, and the chromophores are located in the main chains of polymers. In the last five-year the functional hyperbranched polymers were prepared by an end-capping approach which have attracted more and more attention (18, 19).

Hyperbranched poly(aryl ether ketone) is a type of hyperbranched polymers. Traditionally, it has been prepared by polycondensation reactions of AB_2 monomer which contains one hydroxyl and two fluorine groups (or one fluorine and two hydroxyl groups) (20–25). It's well known that this method is unpractical for the large scale preparation of hyperbranched poly(aryl ether ketone) due to the requirement of special AB_2 monomers. Particularly, the incorporation of the functional group into AB_2 monomer has made the preparation even more difficult (8). In this article, we report the synthesis and characterization of a novel fluoride-terminated hyperbranched poly(ether ether ketone) with phenoxypheyl side group by $A_2 + B_3$ polymerization of 2-(4-phenoxypheny)-1,4-diphenol (A_2) and 1,3,5-tris[4-(4-flourobenzoyl) phenoxy] benzene(B_3), which can be readily modified into the tertiary amino group(-$N(CH_3)_2$) and

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phenyl ethynyl group for fluorescent and self-crosslinking hyperbranched poly(ether ether ketone)s.

2. Experimental

2.1 Materials

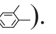
Monomers 1,3,5-tris[4-(4-flourobenzoyl) phenoxy] benzene (B_3), 2-(4-phenoxyphenyl)-1,4-diphenol (A_2), and 4-phenyl ethynyl phenol (PEP) were synthesized as described in (26–28), respectively. m-N,N-Dimethylaminophenol (DMAP) was purchased from Aldrich, and used as received. Tetramethylene sulfone (TMS) was obtained from Jinzhou Oil Refinery of China, and purified by reduced-pressure distillation before use. Anhydrous potassium carbonate, benzene, toluene and N-methy-2-pyrrolidinone (NMP) were purchased from Beijing Chemical Company of China.

2.2 Measurements

Gel-permeation chromatography was carried out with a Waters 410 instrument. The IR spectra were recorded using a Nicolet Impact 410 spectrophotometer. The ^{1}H-NMR spectra were measured with a Bruker 510 spectrometer (500 MHz). Glass transition temperature was determined with a DSC 821^e Mettler Toledo instrument at a heating rate of 10 K/min under N_2. TGA curves were measured with a NetzchSta 449c instrument under the same conditions. The UV and visible were recorded with a Shimadzu UV-2501PC spectrophotometer in THF solutions. The fluorescence spectra were measured with a Perkin-Elmer LS 55 instrument in THF solutions at an exciting radiation wavelength λex 320 ± 10 nm.

2.3 Synthesis and Characterization

2.3.1 Synthesis and Characterization of Fluoride-terminated Hyperbranched Poly(ether ether ketone) with Phenoxypheyl Side Groups (HPEEK-F)

Monomer A_2 (7.20 mmol) and monomer B_3 (10 mmol) were dissolved in teramethylene sulfone (40 ml) in a three-necked flask that was purged with nitrogen, and K_2CO_3 (1.04 g) and toluene (20 ml) were added. The reaction mixture was heated at 140°C for 3 h, toluene was distilled off, and the residue was heated at 220°C for 6 h. The resulting viscous matter was poured into a water-methanol mixture (1:1, vol/vol). The polymer was washed with hot methanol and water and dried at 120°C for 10 h. Yield: 7.83 g, 85%. IR (KBr, cm^{-1}): 1222 cm^{-1} (C-O-C), 3060 cm^{-1} (Ph-H), 1595 cm^{-1} (C-C), 1650 cm^{-1} (C=O), 1112 cm^{-1} (C-F), 923 cm^{-1}, 838 cm^{-1}, and 754 cm^{-1}(). Figure 1 (3) shows the ^{1}H-NMR ($CDCl_3$, δ, ppm): 6.60 (s, 3H), 6.94 (m, 6.03H), 7.11–7.16 (m, 16.2H), 7.23 (m, 1.05H), 7.31 (m, 1.88H), 7.43 (m, 2.02H), 7.72–7.82 (m, 15.6H).

The degree of branching (DB) is a typical characteristic which frequently is being used to evaluate the irregularity of the structure of hyperbranched polymers. In principle, a AB_2 condensation polymerization can give rise to dendritic (D), linear (L) or terminal (T) units. According to the definition given by Frèchet (29), the degree of branching (DB) is calculated by the following equation:

$$DB = (D + T)/(D + T + L) \tag{1}$$

Due to the number of dendritic units is theoretically equal to the number of terminal units at high molecular weights, Hawker and Chu (30) and Frey et al. (31) modified the definition as follows:

$$DB = 2D/(2D + L) \tag{2}$$

The synthesis and characterization of linear and dendritic unit were described in literature (32). Figure 1 (1) and (2) shows the ^{1}H-NMR of linear and dendritic model compounds, respectively. The DB of HPEEK-F calculated to be 0.67 according to Equation (2).

2.3.2 Synthesis and Characterization of Tertiary Amino-terminated Hyperbranched Poly(ether ether ketone) (HPEEK-DMA)

The m-N,N-dimethylaminobenzophenol (DMAP) (3.01 g, 22 mmol), anhydrous K_2CO_3 (1.52 g, 11 mmol), N-methy-2-pyrrolidinone (35 ml) and toluene (25 ml) were added to a 100 ml three-necked flask equipped with a mechanical stirrer, nitrogen inlet with a thermometer, and a Dean-Stark trap with a condenser. The system was allowed to reflux for 4 h, and cooled to room temperature after removal of the toluene. Then 3.50 g of HPEEK-F were added into a reaction mixture. After the addition, the reaction mixture was heated to 160°C for 12 h. The viscous mixture was then cooled to room temperature, and poured into the methanol and water mixture (1:1, vol/vol). The polymer was pulverized in a fine powder by a blender and washed several times with hot methanol and water and dried at 100°C for 10 h. Yield: 4.1 g, 63%. IR (KBr, cm^{-1}): the peaks at 1074 cm^{-1} (-N-C-), 2922 cm^{-1} ($-CH_3$) indicates the existence of amino-terminated HPEEK-DMA. No such absorption bands were found at 1112 cm^{-1} (C-F), and this shows that full modification was achieved. Figure 1 (5) shows the ^{1}H-NMR ($CDCl_3$, δ, ppm): 6.59 (s, 3H), 6.56 (m, 3.31H), 6.40–6.44 (m, 6.45H), 6.93 (m, 9.55H), 7.02–7.10 (m, 23.64H), 7.23 (m, 4.22H), 7.30 (m, 3.32H), 7.43 (m, 3.48H), 7.73–7.81 (m, 22.74H).

2.3.3 Synthesis and Characterization of Phenyl Ethynyl-terminated Hyperbranched Poly(ether ether ketone) (HPEEK-PEP)

The HPEEK-F (3.20 g), anhydrous K_2CO_3 (1.52 g, 11 mmol), 4-phenylethynyl phenol (PEP, 2.10 g, 11 mmol), N-methy-2-pyrrolidinone (35 ml) and benzene (20 ml) were added to 100 ml three-necked flask equipped with a mechanical stirrer, a nitrogen inlet with a thermometer, and a Dean-Stark trap

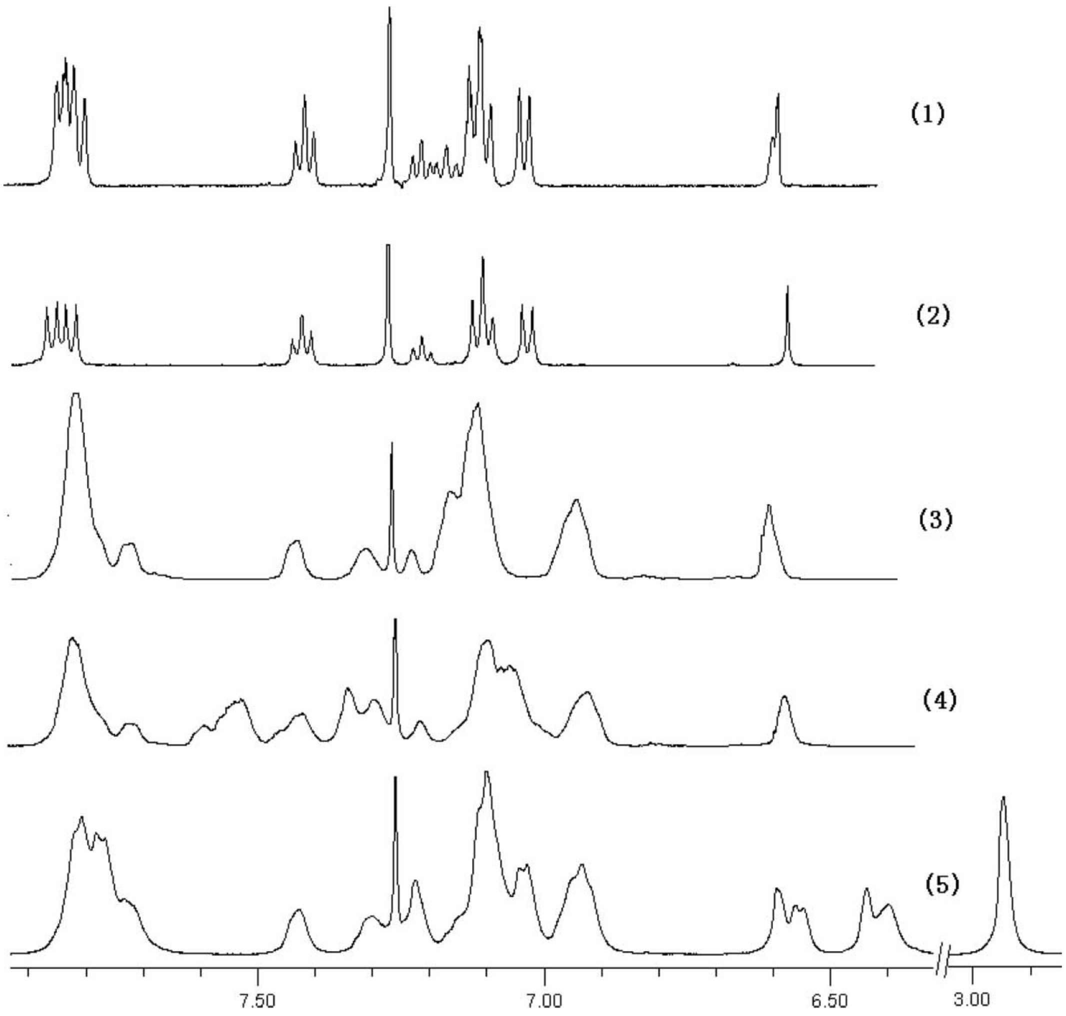


Fig. 1. ^{1}H-NMR spectra of model compounds and hyperbranched poly(ether ether ketone)s. (1) Linear unit; (2) Dendritic unit; (3) HPEEK-F; (4) HPEEK-PEP; (5) HPEEK DMA.

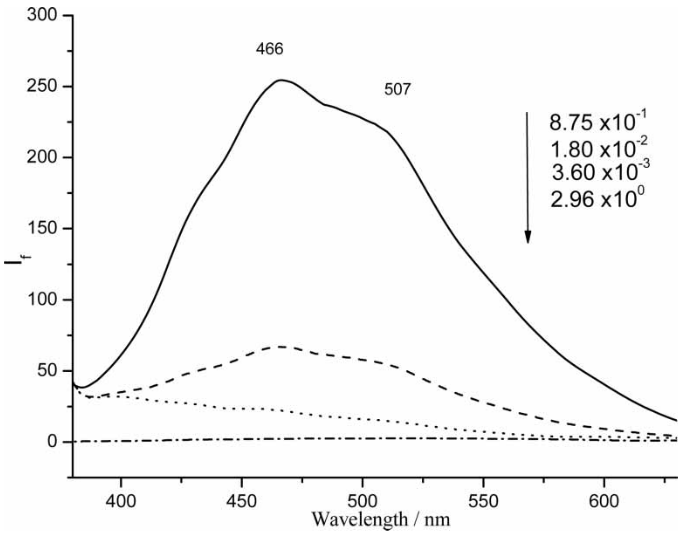


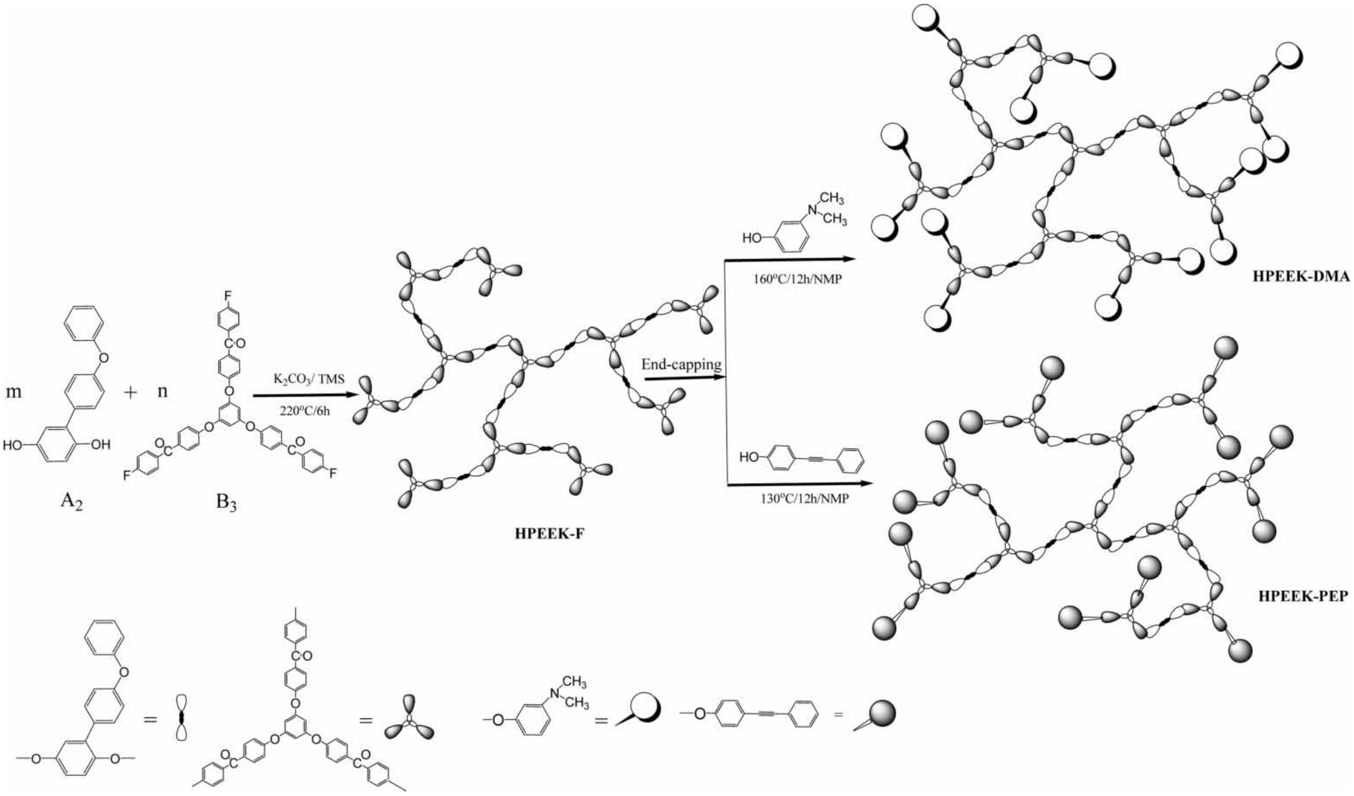
Fig. 2. Effects of concentration on the fluorescence in THF solution, $\lambda_{ex} = 320$ nm.

with a condenser. The system was allowed to reflux at 120°C for 12 h. The purification process of HPEEK-PEP is the same as written above for the HPEEK-DMA. Yield: 4.1 g, 85%. IR (KBr, cm^{-1}): Infirm stretching bands were shown at 2215 cm^{-1} (-C≡C-), and no such absorption bands were found at 1112 cm^{-1} (C-F). This shows that full modification was achieved. Figure 1 (4) shows the ^{1}H-NMR (CDCl$_3$, δ, ppm): 6.59 (s, 3H), 6.93 (m, 6.39H), 7.05–7.11 (m, 20.43H), 7.22 (m, 1.64H), 7.30–7.34 (m, 8.26H), 7.43 (m, 4.01H), 7.52–7.59 (m, 7.33H), 7.72–7.82 (m, 16.03H).

3. Results and Discussion

3.1 Synthesis and Chemical Modification of the Hyperbranche Poly(ether ether ketone)s

Hyperbranched poly(ether ether ketone) with phenoxypheyl side groups (HPEEK-F) has been prepared by using a nucleophilic aromatic substitution reaction, which uses 2-(4-phenoxyphenyl)-1,4-diphenol and 1,3,5-tris[4-(4-flourobenzoyl)



Sch. 1. Synthesis and schematic representation of functional hyperbranched poly(ether ether ketone)s via "$A_2 + B_3$" and end-capping approach.

phenoxy] benzene as the A_2 and B_3 monomers, respectively, as is shown in Scheme 1. This preparation is similar to the preparation of linear poly(ether ether ketone)s. The $A_2 + B_3$ approach involves difficulties in controlling polycondensation reaction due to premature gelation. In order to synthesize high molecular weight polymers, the feed ratio of A_2 to B_3 should be as close to the gel point as possible. The molecular weight of the resulting polymer sample is shown in Table 1. The molecular weight distribution of these hyperbranched poly(aryl ether ketone)s is narrower than that of hyperbranched poly(aryl ether ketone)s, which is prepared by aromatic electrophilic substitution reaction of $A_2 + B_3$ (33).

In the ^{1}H-NMR spectra of the phenyl ethynyl-terminated HPEEK-PEP and tertiary amino-terminated HPEEK-DMA (Fig. 1 (4) and (5)), the substituted phenyl ethynyl proton at 7.52–7.59 ppm and dimethylaminophenoxy proton at 2.95, 6.40–6.44 ppm were observed, respectively. In addition, this typical chemical shift, which had hydrogen protons located in both sides of fluorin atoms, disappeared at 7.16 ppm, further confirms that the chemical modification was achieved completely.

The resulting polymers were soluble in several organic solvents such as THF, DMF, DMAc or $CHCl_3$, but insoluble in apolar organic solvents such as benzene, toluene, acetone and ethanol. These solubility results indicate that the phenoxypheyl side groups in the backbones of hyperbranched polymers significantly affected the solubility. The hyperbranched poly(ether ether ketone)s synthesized from hydroquinone (A_2) and 1,3,5-tris[4-(4-flourobenzoyl) phenoxy] benzene (B_3) are insoluble in organic solvents (34).

Many experiments demonstrated that the nature of terminal functional groups strongly influenced the T_g, solubility and even T_d of the hyperbranched polymer (2). Although HPEEK-F, HPEEK-DMA and HPEEK-PEP have the same backbone

Table 1. Some characteristics of polymers

Polymer	Mn	Mw	Mw/Mn	T_g, (°C)	$T_{d5\%}$, (°C)
HPEEK-F	$8.71 * 10^3$	$1.24 * 10^4$	1.42	105.2	504
HPEEK-DMA	$1.03 * 10^4$	$1.62 * 10^4$	1.57	107.2	416
HPEEK-PEP	$1.01 * 10^4$	$1.77 * 10^4$	1.71	135.5	457
Cured HPEEK-PEP				235.5	472

structure, it was found that the T_g can be varied over a wide range, from 105°C for the HPEEK-F to 13°C for the HPEEK-PEP. The T_d values observed showed obvious changes between HPEEK-F, HPEEK-DMA and HPEEK-PEP. The 5% wt loss which occurred is over 416°C for HPEEK-DMA, while the HPEEK-F is stable up to 500°C. These results show that the nature of the terminal functional groups markedly affects the properties of hyperbranched polymer.

3.2 *Effect of Polymer Concentration and Acidity on the Fluorescence*

The resulting polymers fluoresce blue-green in solid and solution. Absorption maxima are observed in the UV spectra of their solutions in THF at $\lambda = 265$ and 290 nm. Emission spectra, at an exciting radiation wavelength of 320 ± 10 nm, demonstrates two peaks with maxima at 466 and 507 nm.

The HPEEK-DMA shows a "concentration self-quenching effect" in Figure 2. Initially, as the concentration of polymer in the THF solution is increased from 10^{-3} to 10^{-1} g/l, the fluorescence intensity increases, and eventually, completely disappears at [HPEEK-DMA] = 2.96 g/l. However, this type of polymer can easily form intramolecular excimers due to highly branched, three-dimensional structures and the lack of chain entanglements of hyperbranched polymers, it is conceivable that terminal chromophores crowd together on the surface of the polymer, so an excited chromophore can easily interact with another chromophore of the same hyperbranched macromolecules (18).

As the chromophore of the fluorescent polymer carries a tertiary amino group (-$N(CH_3)_2$), and energy migration is possible between the chromophore, fluorescence intensity of the resultant polymer may depend on the acidity of the solution. Figure 3 shows that when pH ≤ 7, the fluorescent intensity increasing trend as the pH increases, the two peaks at 466 nm and 507 nm blue shifts to 423 nm and 462 nm, respectively as the acidity increases. For pH = 6.2, the two peaks at 466 nm and 507 nm merge into one peak at 416 nm. This may be regarded as the formation of a new chromophore group, which ammonium cations formed at the tertiary-amino groups, while the pH decreases.

3.3 *Effect of Curing on the Thermal Properties of HPEEK-PEP*

In this work, DSC analysis was performed to study the effect of curing on the T_g and curing properties of the HPEEK-PEP (Fig. 4). An intense exothermic peak in the first scan was seen due to the reaction of phenyl ethynyl moiety was started at around 310°C and reached maximum at 430°C. As the thermal curing temperature and times increased, after keeping the polymer at 350°C for 3 h or 360°C for 2 h, no further exotherms were observed when the samples were rerun, the T_g increased from 135°C to 235°C. The T_g of the cured HPEEK-PEP from the experiment result is relatively 45°C higher than that of 6F-PEEK-PEP in (35). This attributes to the three-dimensional architecture, and the presence of many terminal groups in hyperbranched polymer leads to higher crosslinking density at the terminal point of polymer, hence, relatively higher T_g than that for the linear polymer.

The thermal stability of these phenyl ethynyl-terminated HPEEK-PEP was investigated by thermal gravimetric analysis under a N_2 atmosphere. After curing the HPEEK-PEP, as shown in Table 1, the polymers showed only 5% wt loss up to 470°C. To examine the gel fraction of the cured polymer, the samples cured at 350°C for 3 h or 360°C for 2 h were extracted with DMF for 5 days and then dried

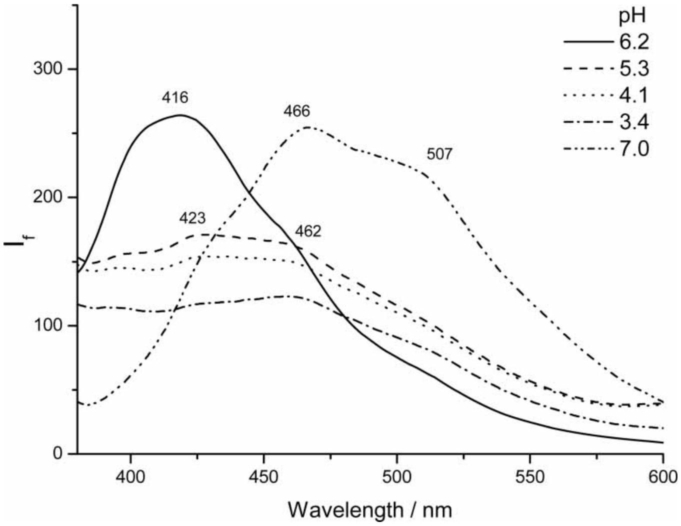


Fig. 3. Curve of fluorescence emission intensity (I_f) at $\lambda_{ex} = 320$ nm as a function of pH.

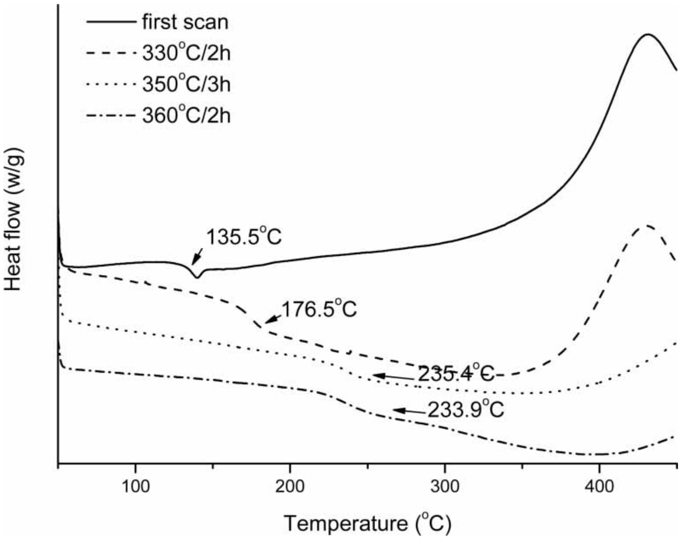


Fig. 4. Effect of the degree of curing on T_g of HPEEK-PEP bearing crosslinkable phenyl ethenyl moiety.

for 5 days at 120°C under vacuum. It was found that the sample did not change the weight by extraction. It seems that the cured sample has a gel faction above 93%. The thermal properties and the formation of the insoluble polymer indicate that the ethynyl group of HPEEK-PEP was thermally reacted with each other by curing.

4. Conclusions

A novel hyperbranched poly(ether ether ketone) containing phenoxypheyl side groups (HPEEK-F) was successfully prepared from 2-(4-phenoxyphenyl)-1,4-diphenol (A_2) and 1,3,5-tris[4-(4-fluorobenzoyl)phenoxy]benzene (B_3) copolymerization.

An end-capping approach was used to synthesize fluorescent (HPEEK-DMA) and self-crosslinking (HPEEK-PEP) hyperbranched poly(ether ether ketone)s. HPEEK-DMA fluoresces blue-green in both solid and in solution. Due to this type of hyperbranched polymer, which contains many chromophores at terminal units of the three-dimensional macromolecules, and lack of chain entanglements in the hyperbranched polymer, can easily result in the formation of intramolecular excimers, the HPEEK-DMA shows a "concentration self-quenching effect". The fluorescence intensity decreased with increments in acidity, furthermore, a blue shift occurred at the two peaks of 466 nm and 507 nm.

After curing, the HPEEK-PEP displayed a T_g at 235.5°C, which is 100°C higher than the original polymer. Thermally cured samples show good anti-chemical corrodibility in DMF, THF, DMAc and NMP solvents.

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